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ANALYTICAL REFERENCE SERVICE TRAINING PROGRAM. REPORT ON WATER METALS NUMBER 2

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

September 1962

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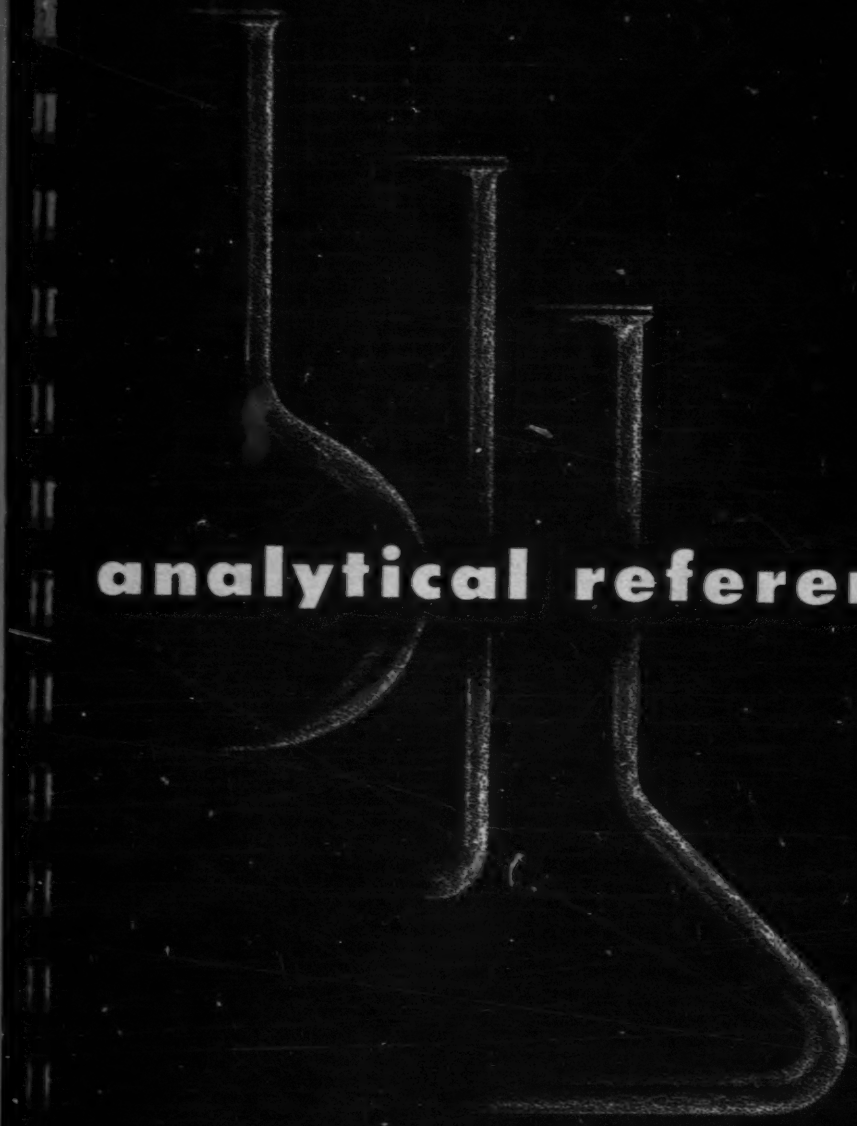

WATER METALS
NUMBER 2
SEPTEMBER, 1962

analytical reference service

TRAINING PROGRAM

Robert A. Taft

SANITARY ENGINEERING CENTER

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CINCINNATI, OHIO

Report

WATER METALS NO. 2

A Study Conducted by the

Analytical Reference Service

TRAINING PROGRAM

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service
Bureau of State Services
Division of Water Supply and Pollution Control

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1962

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ACKNOWLEDGEMENT

The Analytical Reference Service gratefully acknowledges the editorial assistance of Mrs. Marjorie Myers, Publications Editor, Training Program.

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FOREWORD

The Analytical Reference Service is conducted by the Robert A. Taft Sanitary Engineering Center to provide a means of evaluating laboratory methods in the field of environmental sciences and engineering. Membership includes Federal, State, and municipal agencies, industries, universities, consulting firms, and foreign agencies. Cooperative studies by member organizations, through analysis of identical samples of environmental media and critical review of methodology, provide the mechanism for:

Statistical evaluation of procedures, including precision and accuracy.

Comparison of analytical procedures and results between laboratories having similar responsibilities.

Exchange of information regarding method weaknesses.

Improvement of existing methods or development of newer, more accurate methods to replace current procedures.

Development and evaluation of entirely new methodology for the determination of new pollutional components, such as pesticides, herbicides, antimony, cadmium, boron, selenium, phenol, and trace air pollution contaminants.

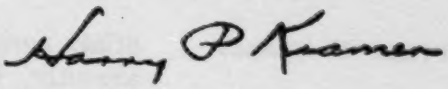
Initially directed toward examination of water, the studies have been broadened to include other media. Samples are designed and prepared to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the staff of ARS, the membership, and consultants. Notice of a study is forwarded to each member with information regarding the qualitative makeup of the sample and special details regarding its handling.

A portion of the sample is shipped to each member who indicates a desire to participate in the study. Accompanying each sample are data forms which provide space for reporting numerical analytical values and a narrative critique of the procedures used. The laboratories are urged to comment on the methods, difficulties, modifications, sources of error, and other factors.

The results and comments of each study are compiled, as in the accompanying report. Experience indicates that a repeat study produces a sizeable increase in the number of participants. In the 1957 water-metals study, 16 agencies participated; 66 agencies have cooperated in this study.

The selection of studies is guided by answers to the questionnaires distributed to member agencies to poll their interests. Results of this poll continue to serve as a useful aid in planning future studies.

Membership now consists of 152 agencies of diversified interests, with foreign interest increasing rapidly. The assistance and experience that agencies from other countries can bring to this program will be invaluable to the entire membership.



H. P. Kramer
Chief, Training Program

STUDIES ON WHICH REPORTS HAVE BEEN COMPLETED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. First study completed in 1957. Report on second study to be distributed in the near future.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation using a specified procedure. Studies completed in 1958 and 1961.
Water-Radiological	Gross beta and gamma activity. Studies completed in 1959 and 1961.
Water-Surfactant	Surfactant in various waters. Study completed in 1959.
Water Oxygen-Demand	Biochemical oxygen demand and chemical oxygen demand. Study completed in 1960.
Water Trace-Elements	Study completed in 1962. Constituents were arsenic, boron, selenium, and beryllium.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass fiber hi-vol filter mats. Study completed in 1958.
Air-Lead	Filter paper tape impregnated with lead. Study completed in 1961.
Milk DDT-Residue	Study completed in 1962. Quantitative determination of DDT in milk.

PARTICIPANTS IN THIS STUDY

Arizona State Department of Health
California Department of Water Resources
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Water Service Company, San Jose
Case Institute of Technology, Department of Civil and Sanitary Engineering
Colorado State Department of Public Health
Connecticut State Department of Health
Chicago Department of Water and Sewers, South District Filtration Plant
City of Durham Department of Water Resources
Columbia University, Plainsboro, New Jersey
Culligan, Inc., Northbrook, Illinois
Dearborn Chemical Company, Chicago, Illinois
E. I. du Pont de Nemours & Co., Aiken, South Carolina
Flint Water Plant, Department of Public Works and Utilities
Florida State Board of Health (Sanitary Engineering, Jacksonville)
Florida State Board of Health (Winter Haven)
Hagan Chemicals & Controls, Inc., Pittsburgh, Pennsylvania
Illinois State Department of Public Health (Springfield)
Illinois State Water Survey Division
Indiana State Board of Health
Kentucky State Department of Health
Kennecott Copper Corporation, St. Louis, Missouri
Louisiana State Board of Health
Los Angeles County Flood Control District
Los Angeles Department of Public Works (Hyperion Treatment Plant)
Los Angeles Department of Water and Power
Maryland State Department of Health
Metropolitan Water District of Southern California
Michigan Water Resources Commission
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
New Jersey State Department of Health
New York State Conservation Department
North Carolina Department of Water Resources
Ohio State Department of Health

Omaha Metropolitan Utilities District
Oregon State Board of Health
Ottawa, Ontario, Canada, Occupational Health Division, Department of National Health and Welfare
Pearl Harbor Naval Shipyard
Pennsylvania Department of Health
Philadelphia Suburban Water Company
Philadelphia Water Department (Belmont Laboratory)
Radiation Detection Company, Palo Alto, California
Rhode Island Department of Health
Sandia Corporation, Sandia Base, Albuquerque, New Mexico
South Carolina Water Pollution Control Authority
St. Louis County Water Company
Tennessee Stream Pollution Control Board
Texas State Department of Health
2794th U. S. Air Force Dispensary - Class B
University of Pittsburgh, Graduate School of Public Health
U. S. Army Environmental Hygiene Agency, Maryland
U. S. Department of the Interior, Bureau of Reclamation, Denver, Colorado
U. S. Department of the Interior, Geological Survey, Sacramento, California
U. S. Department of the Interior, Geological Survey, Denver, Colorado
U. S. Department of the Interior, Geological Survey, Columbus, Ohio
Utah State Department of Health
Vancouver, B. C., Canada, Department of National Health and Welfare
Vermont State Department of Health
Virginia State Department of Health
Washington State Department of Health
Wisconsin State Board of Health

WATER-METALS NUMBER 2

PURPOSE OF STUDY

The Water-Metals No. 2 study is similar in design to the previous study of this type conducted in 1957. Request for the study came from a number of Analytical Reference Service members who desired an opportunity for comparison of individual laboratory results and for further evaluation of current procedures. The greatly enlarged ARS membership and the publication of the 11th edition of Standard Methods have opened the way for a more comprehensive survey of methods currently in use on a national basis. The recent release of new Public Health Service Drinking Water Standards makes this report timely because it defines some of the problems associated with the detection and measurement of small concentrations of metals in water. Each metal in the sample was determined by a number of methods, permitting comparative evaluations.

PREPARATION OF SAMPLE

The sample substrate consisted of 400 liters of distilled deionized water to which the following metallic compounds were added:

Salt	mg/l of metal		Av. ARS Lab. Analysis	
$AlCl_3 \cdot 6H_2O$	1.80	(Al)	2.18	(Aluminon)
$K_2Cr_2O_7$	0.18	(Cr)	0.15 0.17	(Lieber) (Polarograph)
$CuSO_4 \cdot 5H_2O$	0.42	(Cu)	0.42 0.43	(Cuprethol) (Polarograph)
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	0.62	(Fe)	0.63	(1, 10-Phenanthroline)
$MnSO_4 \cdot H_2O$	0.25	(Mn)	0.30	(Periodate)
$Cd(NO_3)_2 \cdot 4H_2O$	0.24	(Cd)	0.25 0.24	(Dithizone) (Polarograph)
$ZnSO_4 \cdot 7H_2O$	0.90	(Zn)	1.07 0.90	(Dithizone-Mixed Color) (Polarograph)
$Pb(NO_3)_2$	0.18	(Pb)	0.18 0.14	(Dithizone-Mixed Color) (Polarograph)

The sample had a pH of 3.1. It was shipped in polyethylene bottles in April, 1961.

Only the average concentrations found by the ARS laboratory are reported, as its function is only to confirm the theoretical concentrations. It may be noted that the values obtained follow the trend toward high or low results as shown in the bar charts. Since the sample contained the highest grade chemicals and the calculations were checked by several staff members, the deviations from the theoretical are generally viewed as inherent weaknesses in the analytical methods used. The iron results are an exception to this conclusion and are discussed in detail.

TREATMENT OF THE DATA

The participating agencies reported a total of 1,199 analytical results based on measurements made in triplicate. In the tabulation, laboratory precision is shown by the average percent deviation of each agency's replicate results from their mean. Accuracy is indicated by the average percent deviation of each agency's results from the amount added. The multiplicity of references cited for each determination would make statistical evaluation meaningless if each reference were treated as a separate method. The various procedures, therefore, were grouped according to the basic reactions, and slight modifications in technique were not considered in the evaluation. Some agencies failed to identify completely the analytical method used and/or neglected to cite an adequate reference. To utilize the data as fully as possible, an extensive literature search was required and some assumptions were necessary.

The standard deviations were calculated by using the difference between the separate results and the mean. All reported values were retained regardless of the magnitude of deviation.

To relate the accuracy of the methods more directly to the agencies performing the determination, the term "50% range" is used. This range is defined as the maximum deviation from the amount of material added for the more accurate half (50%) of all results for each measurement. For example, on the copper determination the range for 67 laboratories was $\pm$ 1.08 mg/l, but at least 34 (50%) laboratories reported values within $\pm$ 0.06 mg/l of the true value. Early in the ARS program, consultation with the members produced agreement that a 50% range would be a reasonable goal for accuracy for subsequent determi- by member laboratories.

Since the instruction sheet carries the request that results be reported to the nearest hundredth mg/l, the values reported to three decimal places were rounded off for uniformity, using the rule in Standard Methods.

Average reported values are shown in the bar charts, and the different analytical methods employed are identified.

Aluminum (1.80 mg/l)

Due to its widespread use in water treatment and its abundance in the earth's crust, the determination of aluminum is of considerable interest.

The "Aluminon" procedure recommended by Standard Methods is the principal method used for this determination. The overwhelming majority of results obtained by this method, compared with the few results obtained by other procedures, makes a statistical evaluation inconclusive. Nearly all results are high, showing generally poor accuracy. The Aluminon results, however, are normally distributed and are fairly precise, as shown by the standard deviation of $\pm$ 0.137. The ortho-phenanthroline procedure produces approximately the same degree of accuracy and precision, according to the six results reported by two laboratories. The Eriochrome Cyanine R procedure seems to be as accurate but less precise, based on six results from two laboratories.

On the basis of the few results obtained by gravimetric analysis and by the spectrograph, these methods would not be suitable for aluminum measurement at the concentration present in this sample, as both accuracy and precision are lacking. One spectrographic result was reported between 2 and 10 mg/l and, therefore, was not used in the statistical evaluation.

The 1957 Water Metals study showed the same trend toward high results for aluminum, with a mean value 72% higher than the amount added. Although the present study indicates considerable improvement in accuracy with an overall mean value only 23% high, it still appears that a more reliable method is needed.

ALUMINUM

Summary of Data (Amount added 1.80 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Aluminon	37	108	2.09	2.14	0.56-2.90	± 0.40	± 0.137	± 0.026
ECR	2	6	2.05	2.04	1.67-2.45	± 0.13	± 0.390	± 0.409
Ortho-phenanthroline	2	6	2.12	2.06	1.98-2.40	± 0.23	± 0.163	± 0.171
Gravimetric	3	5	4.43	4.00	0.72-8.53	± 2.20	± 3.691	± 4.583
Spectrograph	2	3	2.67	2.50	1.80-3.70	± 0.70	± 0.961	± 2.387
Overall	47	131	2.21	2.15	0.56-8.53	± 0.40	± 0.903	± 0.156

Table 1. ALUMINUM (Amount added = 1.80 mg/l)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
8112	0.56 0.58 0.58	0.57	1.75	68.33	Aluminon [1]
7722	0.72	0.72	-----	60.00	Gravimetric
5111	1.30 1.33 1.33	1.32	1.01	26.67	Aluminon [1]
1711(b)	0.80 2.00 1.80	1.50	33.33	16.67	Aluminon [1]
5811	1.67 1.72 1.70	1.70	0.98	5.56	Eriochrome Cyanine R
4811	1.75 1.70 1.75	1.73	1.35	3.89	Aluminon [1]
6311	1.81 1.84 1.71	1.79	2.79	0.56	Aluminon [1,34]

Table 1 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1311	1.83 1.83 1.74	1.80	2.22	0	Aluminon
1711(a)	2.50 2.40 0.64	1.80	45.56	0	Aluminon
7112(a)	1.80	1.80	-----	0	Aluminon
7112(b)	1.80	1.80	-----	0	Spectrographic
8512	1.82 1.84 1.88	1.86	1.44	3.33	Aluminon
4711	1.96 1.90 1.88	1.91	1.57	6.11	Aluminon
4321	2.00 2.00 2.00	2.00	0	11.11	Aluminon
8423	1.98 1.98 2.03	2.00	1.16	11.11	Ferron-Ortho-Phenanthroline

Table 1 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
1611	1.92 2.00 2.12	2.01	3.48	11.67	Aluminon	1
7222	1.94 2.05 2.14	2.04	3.43	13.33	Aluminon	1
1711(c)	2.10 1.88 2.20	2.06	5.82	14.44	Aluminon	1
3226	2.15 2.00 2.05	2.07	2.74	15.00	Aluminon	1
9613	2.00 2.12 2.12	2.08	2.56	15.56	Aluminon	1
3526	2.10 2.10 2.10	2.10	0	16.67	Aluminon	5
2611	2.14 2.14 2.12	2.13	0.47	18.83	Aluminon	1

Table 1 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
7912	2.05 2.09 2.30	2.15	4.80	19.44	Aluminon [1]
6512	2.18 2.15 2.15	2.16	0.62	20.00	Aluminon [1]
8222	2.10 2.30 2.10	2.16	4.01	20.00	Aluminon [1]
2926	2.20 2.25 2.12	2.19	2.13	21.67	Aluminon [1]
1115	2.20 2.20 2.20	2.20	0	22.22	Aluminon [1]
5511	2.20 2.20 2.25	2.22	1.05	23.33	Aluminon [1]
9113	2.10 2.40 2.20	2.23	4.93	22.22	Ferron-Ortho-Phenanthroline [39]

Table 1 (Continued)

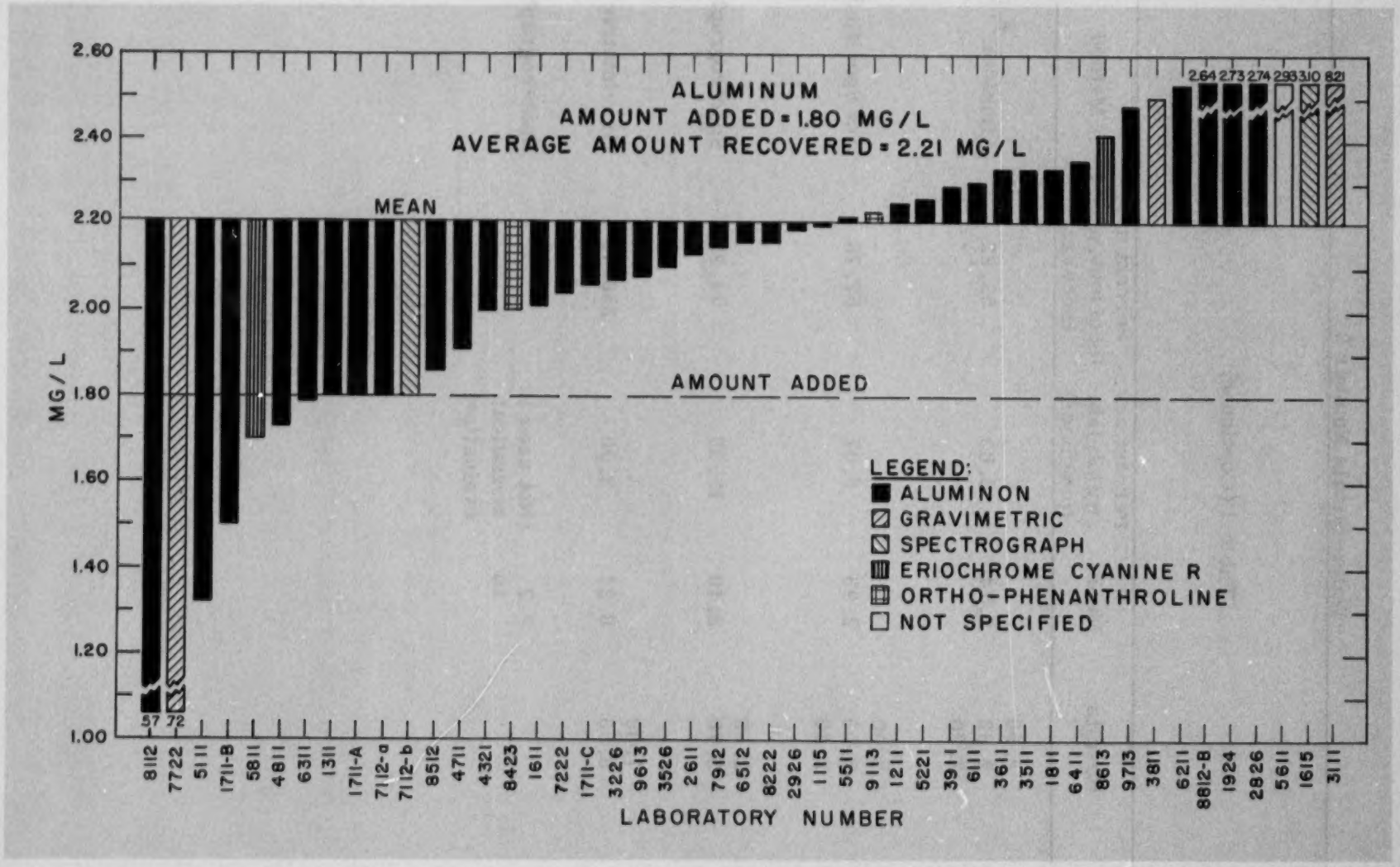
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1211	2.23 2.23 2.30	2.25	1.33	25.00	Aluminon [1]
5221	2.24 2.30 2.24	2.26	1.18	25.56	Aluminon [5]
3911	2.00 2.44 2.44	2.29	8.56	26.11	Aluminon [12]
6111	2.40 2.20 2.30	2.30	2.90	27.78	Aluminon [1]
3611	2.30 2.30 2.40	2.33	1.86	29.44	Aluminon [1]
3511	2.40 2.30 2.30	2.33	1.86	29.44	Aluminon [1]
1811	2.30 2.30 2.38	2.33	1.58	29.44	Aluminon [1]

Table 1 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6411	2.38 2.31 2.36	2.35	1.14	30.56	Aluminon [1]
8613	2.35 2.42 2.45	2.41	1.52	33.89	Eriochrome Cyanine R [38]
9713	2.45 2.60 2.40	2.48	3.09	37.78	Aluminon [1]
3811	4.00 1.00	2.50	60.00	38.89	Gravimetric
6211	2.60 2.50 2.50	2.53	1.71	40.56	Aluminon [5]
8812-B	2.70 2.58	2.64	2.27	46.67	Aluminon [1]
1924	2.70 2.70 2.80	2.73	1.59	51.67	Aluminon [1]

Table 1 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
2826	2.90 2.62 2.70	2.74	3.89	52.22	Aluminon [5,13]
5611	3.00 3.00 2.80	2.93	3.07	62.78	Not Specified
1615	2.50 3.70	3.10	19.35	72.22	Spectrographic
3111	7.89 8.53	8.21	3.90	356.11	Gravimetric [17]
1215		> 2 10	(Not used in statistical evaluation)		Spectrographic


ALUMINUM
AMOUNT ADDED = 1.80 MG/L
AVERAGE AMOUNT RECOVERED = 2.21 MG/L
MEAN
AMOUNT ADDED
MG/L
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
LEGEND:
ALUMINON
GRAVIMETRIC
SPECTROGRAPH
ERIOCHROME CYANINE R
ORTHO-PHENANTHROLINE
NOT SPECIFIED
2.64 2.73 2.74 2.93 3.10 8.21
.57 .72
8112 7722 5111 1711-B 5811 4811 6311 1311 1711-A 7112-a 7112-b 8512 4711 4321 8423 1611 7222 1711-C 3226 9613 3526 2611 7912 6512 8222 2926 1115 5511 9113 1211 5221 3911 6111 3611 3511 1811 6411 8613 9713 3811 6211 8812-B 1924 2926 5611 1615 3111
LABORATORY NUMBER

Chromium (0.18 mg/l)

Diphenylcarbazide was the only colorimetric reagent used for the measurement of chromium. The various procedures differ only in the method of oxidizing chromium to the hexavalent form necessary for the color reaction.

The data show that the results are generally below the amount added. Although the metal was added as hexavalent chromium in the form of potassium dichromate, results from one laboratory which employed the method for hexavalent chromium were zero. Apparently the metal reverted to the trivalent state under the acid conditions of the sample. Failure to recover the theoretical amount of chromium may have been due to incomplete oxidation, volatilization during digestion periods, or loss by adsorption onto the walls of the polyethylene container.

To evaluate the overall performance more realistically, the extremely high results reported by one agency using a spectrograph were discarded. This refinement has the effect of reducing the overall mean from 0.17 mg/l to 0.14 mg/l. The overall precision, as indicated by the standard deviation, was accordingly improved from $\pm$ 0.279 mg/l to $\pm$ 0.057.

More than half of the participants used the Permanganate-Azide procedure, which appears to be slightly more precise than the other procedures specified. No significant difference in accuracy is apparent. Of three laboratories using the spectrograph, two reported nearly perfect results, but the values reported by the third were discarded, as explained above.

CHROMIUM

Summary of Data (Amount added 0.18 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Permanganate Azide	30	89	0.14	0.14	0.04 - 0.24	± 0.05	± 0.039	± 0.008
Alkaline Hypobromite	12	36	0.15	0.14	0.10 - 0.34	± 0.05	± 0.059	± 0.020
Ammonium Persulfate	1	3	0.14	0.14	0.12 - 0.15	± 0.04	± 0.048	± 0.119
Hexavalent Chromium	1	3	0	0	0	--	--	--
Diphenylcarbazide with unspecified oxidation	2	5	0.16	0.16	0.15 - 0.18	± 0.02	± 0.015	± 0.092
Diphenylcarbazide Unspecified	3	9	0.14	0.15	0.12 - 0.16	± 0.03	± 0.057	± 0.044
Spectrograph	3	6	0.95	0.18	0.15 - 3.00	± 0.00	± 1.243	± 1.305
Not identified	1	3	0.37	0.36	0.36 - 0.40	± 0.18	± 0.073	± 0.181
Overall	53	154	0.17	0.14	0.00 - 3.00	± 0.05	± 0.279	± 0.044
Refined overall	52	152	0.14	0.14	0.00 - 0.40	± 0.05	± 0.057	± 0.009

Table 2. CHROMIUM (0.18 mg/l added)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
2826	0.00 0.00 0.00	0.00	0.00	100.0	Hexavalent method with diphenyl-carbazide
1711(b)	0.05 0.04 0.04	0.04	8.25	75.88	Permanganate-Azide
1711(a)	0.12 0.06 0.06	0.08	33.25	55.55	Permanganate-Azide
3911	0.09 0.09 0.09	0.09	0.00	50.0	Permanganate-Azide
7912	0.09 0.10 0.11	0.10	6.66	44.44	Permanganate-Azide
1311	0.11 0.11 0.12	0.11	3.00	37.00	Alkaline Hypobromite
5511	0.10 0.11 0.11	0.11	3.00	40.72	Alkaline Hypobromite

Table 2 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
9613	0.12 0.10 0.10	0.11	9.09	40.74	Permanganate-Azide
1811	0.11 0.11 0.11	0.11	0.00	38.89	Permanganate-Azide
2611	0.11 0.11 0.10	0.11	3.00	40.74	Permanganate-Azide
9713	0.11 0.11 0.12	0.11	3.00	37.03	Permanganate-Azide
1611	0.12 0.11 0.12	0.12	2.78	35.18	Alkaline Hypobromite
2111	0.15 0.10 0.10	0.12	19.42	35.17	Permanganate-Azide
3511	0.12 0.12 0.12	0.12	0.00	33.33	Unspecified Diphenylcarbazide

Table 2 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
7522	0.12 0.12 0.12	0.12	0.00	33.33	Permanganate-Azide [1]
8613	0.12 0.12 0.12	0.12	0.00	33.33	Permanganate-Azide [39]
4421	0.12 0.12 0.12	0.12	0.00	33.33	Permanganate-Azide [1]
5711	0.12 0.12 0.12	0.12	0.00	33.33	Permanganate-Azide [1]
1924	0.13 0.13 0.12	0.13	2.54	29.61	Alkaline Hypobromite [1]
2411	0.13 0.13 0.14	0.13	2.54	25.94	Alkaline Hypobromite [1]
3111	0.13 0.13 0.13	0.13	0.00	27.78	Permanganate-Azide [1]

Table 2 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
4711	0.12 0.14 0.14	0.13	7.69	25.94	Permanganate-Azide [1]
6411	0.12 0.14 0.15	0.14	7.14	24.06	Diphenylcarbazide-Ammonium persulfate oxidation
4811	0.15 0.14 0.13	0.14	4.78	22.22	Alkaline Hypobromite [5]
1911	0.14 0.14 0.14	0.14	0.00	22.22	Alkaline Hypobromite [1]
4321	0.13 0.14 0.15	0.14	4.78	22.22	Permanganate-Azide
6311(a)	0.15 0.14 0.14	0.14	2.36	20.39	Permanganate-Azide [1,32]
8512	0.14 0.14	0.14	0.00	22.22	Permanganate-Azide [32]

Table 2 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
4511	0.15 0.15 0.15	0.15	0.00	16.67	Permanganate-Azide
7222	0.16 0.15 0.15	0.15	2.20	14.83	Alkaline Hypobromite
2926	0.15 0.15 0.15	0.15	0.00	16.67	Permanganate-Azide
1211	0.15 0.15 0.15	0.15	0.00	16.67	Alkaline Hypobromite
2211	0.15 0.15 0.15	0.15	0.00	16.67	Permanganate-Azide
3226	0.15 0.16 0.15	0.15	2.20	14.83	Diphenylcarbazide with unspecified oxidation
5811	0.15 0.15 0.15	0.15	0.00	16.67	Unspecified with diphenylcarbazide

Table 2 (Continued)

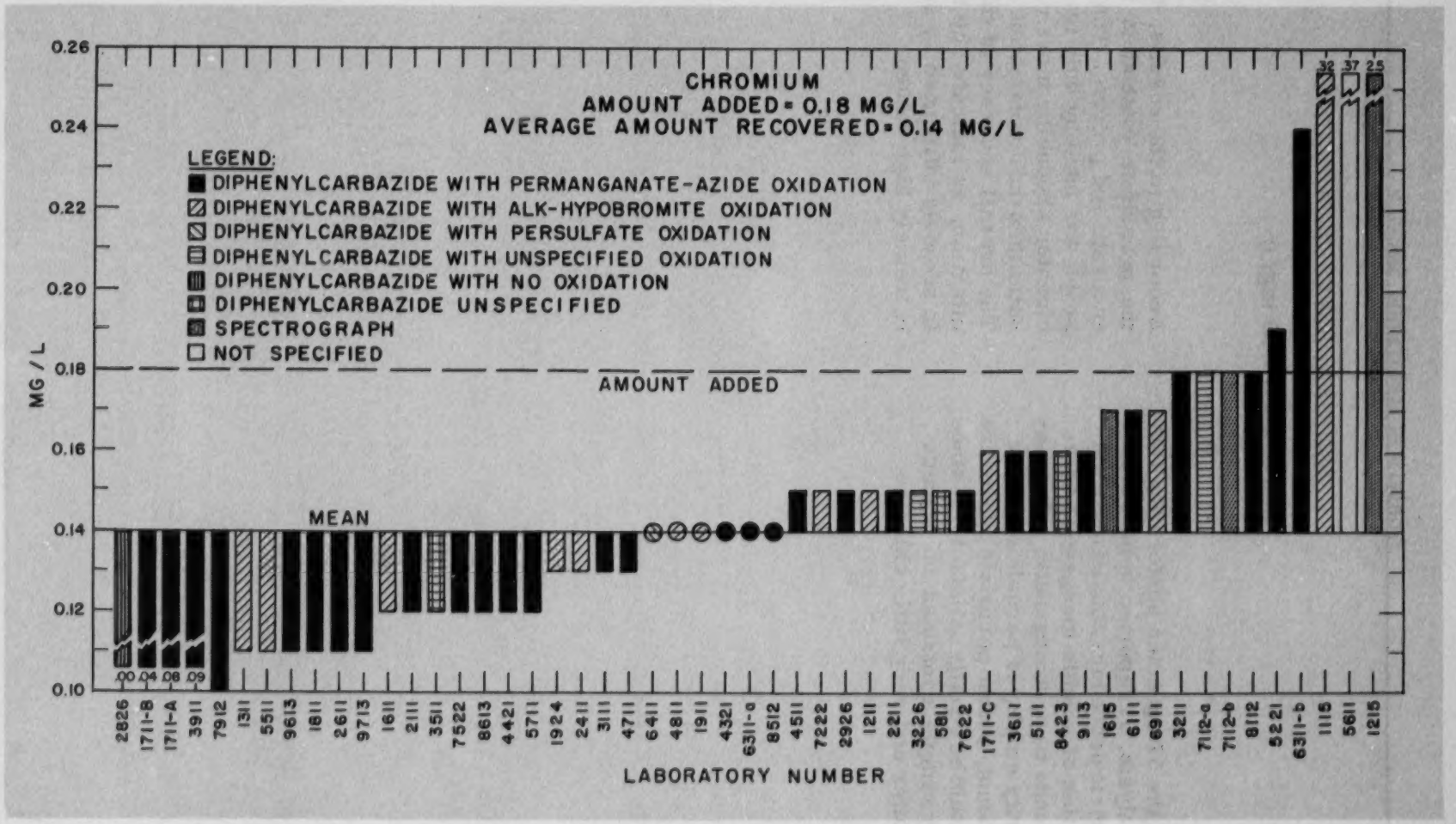
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
7622	0.16 0.13 0.15	0.15	6.67	18.50	Permanganate-Azide [1]
1711(c)	0.11 0.12 0.26	0.16	39.56	38.89	Alkaline Hypobromite [1]
3611	0.16 0.16 0.16	0.16	0.00	11.11	Permanganate-Azide [9,21]
5111	0.16 0.17 0.15	0.16	4.19	11.11	Permanganate-Azide [32]
8423	0.16 0.16 0.16	0.16	0.00	11.11	Unspecified diphenylcarbazide modification
9113	0.16 0.16 0.16	0.16	0.00	11.11	Permanganate-Azide [39]
1615	0.18 0.18 0.15	0.17	7.82	5.56	Spectrographic

Table 2 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6111	0.15 0.18 0.18	0.17	7.82	5.56	Permanganate-Azide [1]
6911	0.17 0.18 0.15	0.17	5.88	7.39	Alkaline Hypobromite [1,27]
3211	0.18 0.19 0.16	0.18	5.56	5.56	Permanganate-Azide [1]
7112 (a)	0.18 0.18	0.18	0.00	0.00	Unspecified diphenylcarbazide oxidation method
7112 (b)	0.18	0.18	----	0.00	Spectrographic
8112	0.20 0.18 0.16	0.18	7.39	7.39	Permanganate-Azide [1]
5221	0.20 0.18 0.20	0.19	5.26	7.39	Permanganate-Azide [1]
6311(b)	0.24 0.24 0.24	0.24	0.00	33.33	Permanganate-Azide [1,32]

Table 2 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1115	0.34 0.32 0.30	0.32	4.16	77.78	Alkaline Hypobromite
5611	0.40 0.36 0.36	0.37	4.51	107.38	Not specified
1215	3.0 2.0	2.5	20.00	1288.89	Spectrographic


CHROMIUM
AMOUNT ADDED = 0.18 MG/L
AVERAGE AMOUNT RECOVERED = 0.14 MG/L
LEGEND:
DIPHENYLCARBAZIDE WITH PERMANGANATE-AZIDE OXIDATION
DIPHENYLCARBAZIDE WITH ALK-HYPOBROMITE OXIDATION
DIPHENYLCARBAZIDE WITH PERSULFATE OXIDATION
DIPHENYLCARBAZIDE WITH UNSPECIFIED OXIDATION
DIPHENYLCARBAZIDE WITH NO OXIDATION
DIPHENYLCARBAZIDE UNSPECIFIED
SPECTROGRAPH
NOT SPECIFIED
AMOUNT ADDED
MEAN
MG/L
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
.00 .04 .08 .09
32 37 25
2826 1711-B 1711-A 3911 7912 1311 5511 9613 1811 2611 9713 1611 2111 3511 7522 8613 4421 5711 1924 2411 3111 4711 6411 4811 1911 4321 6311-a 8512 4511 7222 2926 1211 2211 3226 5811 7622 1711-C 3611 5111 8423 9113 1615 6111 6911 3211 7112-a 7112-b 8112 5221 6311-b 1115 5611 1215
LABORATORY NUMBER

Manganese (0.25 mg/l)

Of the 57 agencies performing this analysis, 51 reported using a colorimetric procedure consisting of oxidation of soluble manganous compounds to permanganate. The majority employed persulfate as the oxidant, but the periodate procedure should be equally satisfactory, since the sample contained no organic matter and very little chloride.

According to the results, however, the persulfate method is more accurate and precise. The spectrograph was used by only two participants, producing more erratic results than the colorimetric methods. The overall accuracy of this determination, as indicated by the mean, is strongly influenced by several extremely high values.

MANGANESE

Summary of Data (Amount Added 0.25 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Persulfate	32	93	0.27	0.25	0.10 - 0.67	± 0.03	± 0.100	± 0.021
Periodate	19	57	0.29	0.25	0.16 - 1.20	± 0.04	± 0.181	± 0.048
Spectrograph	2	4	0.35	0.32	0.25 - 0.50	± 0	± 0.120	± 0.191
Overall	57	166	0.28	0.25	0.10 - 1.20	± 0.03	± 0.131	± 0.020

Table 3. MANGANESE (Amount added = 0.25 mg/l)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
2336	<0.1	---	---	---	Periodate [8]
2111	0.10 0.10 0.14	0.11	15.18	56.00	Persulfate [1]
1924	0.19 0.20 0.19	0.19	1.74	24.00	Persulfate [5]
8423	0.22 0.16 0.19	0.19	10.53	24.00	Periodate
9223	0.19 0.19 0.20	0.19	1.74	24.00	Periodate [1]
2411	0.21 0.19 0.19	0.20	5.00	20.00	Periodate [1]
4711	0.20 0.20 0.20	0.20	0.00	20.00	Periodate [1]

Table 3 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
5311	0.20 0.20 0.20	0.20	0.00	20.00	Persulfate [1]
4511	0.21 0.22 0.20	0.21	3.19	16.00	Periodate [1]
3211	0.20 0.20 0.23	0.21	6.33	16.00	Persulfate [1]
7522	0.22 0.21 0.21	0.21	1.57	16.00	Periodate [1]
8613	0.21 0.23 0.21	0.22	4.54	12.00	Periodate [39]
4811	0.22 0.22 0.22	0.22	0.00	12.00	Persulfate [5]
6211	0.22 0.22 0.22	0.22	0.00	12.00	Persulfate [1]

Table 3 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
3111	0.22 0.22 0.22	0.22	0.00	12.00	Periodate [1]
5221	0.22 0.22 0.23	0.22	1.50	12.00	Persulfate [5]
1311	0.23 0.23 0.23	0.23	0.00	8.00	Periodate [1]
6411	0.25 0.23 0.23	0.24	4.17	4.00	Persulfate [1]
1211	0.23 0.23 0.25	0.24	4.17	4.00	Persulfate [1]
5811	0.24 0.24 0.24	0.24	0.00	4.00	Persulfate
7112 (a)	0.24	0.24	---	4.00	Persulfate [1]
7622	0.24 0.23 0.24	0.24	1.38	4.00	Persulfate [1]

Table 3 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
8512	0.24 0.24	0.24	0.00	4.00	Persulfate	1
6512	0.25 0.25 0.25	0.25	0.00	0.00	Periodate	1
7112(b)	0.25	0.25	---	0.00	Spectrograph	
1811	0.25 0.25 0.25	0.25	0.00	0.00	Persulfate	1
2211	0.25 0.25 0.25	0.25	0.00	0.00	Periodate	6
7912	0.25 0.25 0.25	0.25	0.00	0.00	Periodate	1
9713	0.25 0.26 0.25	0.25	1.32	0.00	Periodate	1
1711(c)	0.20 0.30 0.30	0.26	17.96	4.00	Persulfate	1

Table 3 (Continued)

Lab No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
5511	0.27 0.27 0.25	0.26	3.85	4.00	Unspecified	1
5611	0.30 0.28 0.20	0.26	15.38	4.00	Unspecified	
1911	0.26 0.26 0.26	0.26	0.00	4.00	Persulfate	1
3526	0.20 0.30 0.30	0.26	17.96	4.00	Periodate	5
4321	0.26 0.26 0.26	0.26	0.00	4.00	Periodate	
4421	0.25 0.26 0.27	0.26	2.58	4.00	Persulfate	1
5711	0.25 0.27 0.27	0.26	3.85	4.00	Persulfate	1

Table 3 (Continued)

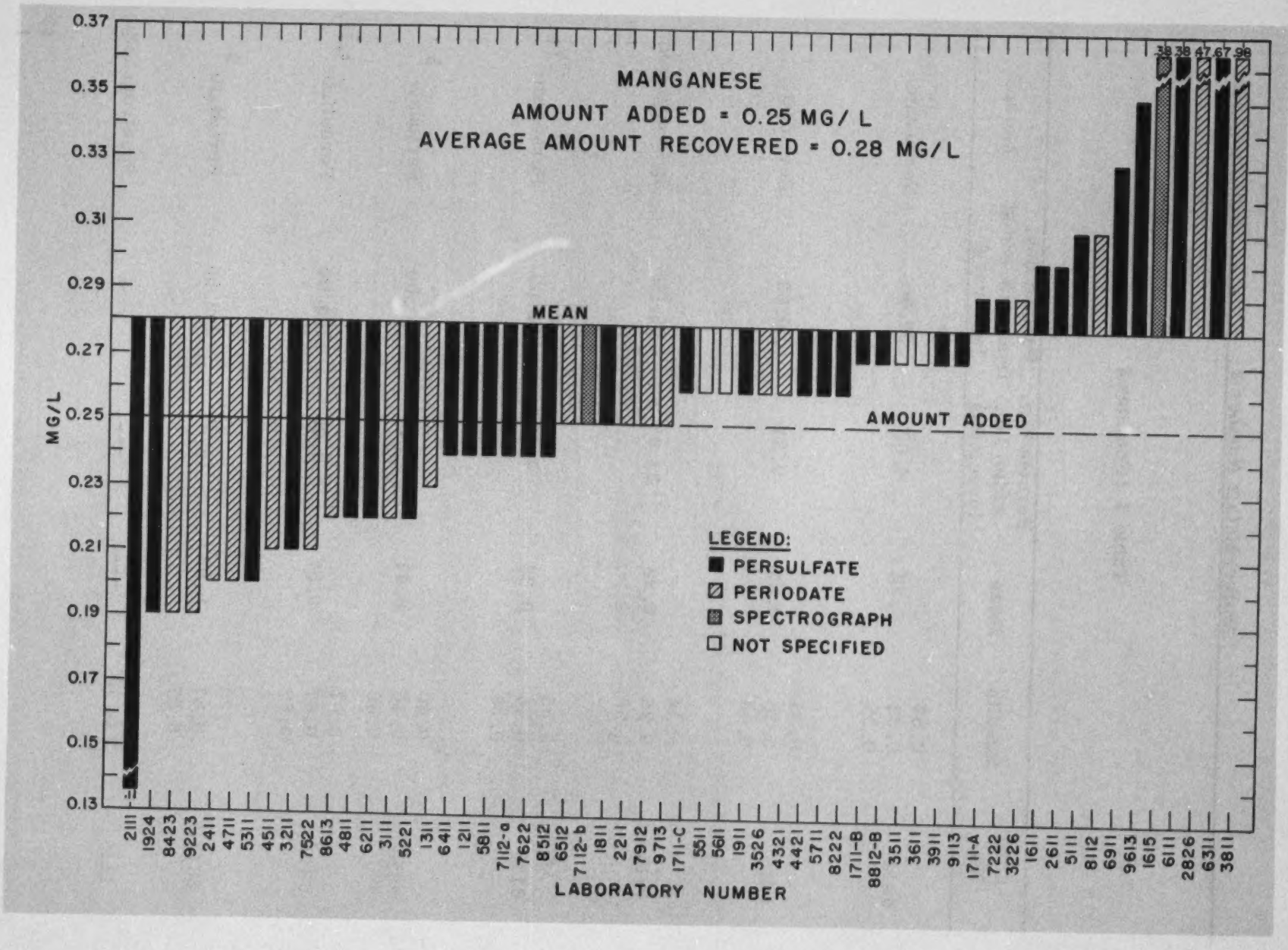
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
8222	0.24 0.28 0.26	0.26	5.12	4.00	Persulfate	1
1711(b)	0.15 0.30 0.35	0.27	28.41	8.00	Persulfate	1
8812(b)	0.28 0.26 0.26	0.27	3.70	8.00	Persulfate	5
3511	0.25 0.30 0.25	0.27	8.63	8.00	Unspecified	1
3611	0.28 0.27 0.25	0.27	3.70	8.00	Unspecified	1
3911	0.30 0.27 0.25	0.27	6.18	8.00	Persulfate	1
9113	0.25 0.25 0.30	0.27	8.63	8.00	Persulfate	39

Table 3 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Methods
1711(a)	0.23 0.30 0.33	0.29	12.66	16.00	Persulfate [1]
7222	0.32 0.25 0.29	0.29	8.03	16.00	Persulfate [1]
3226	0.28 0.30 0.30	0.29	3.45	16.00	Periodate [1]
1611	0.30 0.30 0.30	0.30	0.00	20.00	Persulfate [1]
2611	0.30 0.30 0.31	0.30	1.10	20.00	Persulfate [3]
5111	0.31 0.31 0.31	0.31	0.00	24.00	Persulfate [5]
8112	0.32 0.33 0.28	0.31	6.45	24.00	Periodate [1]

Table 3 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6911	0.32 0.32 0.35	0.33	4.03	32.00	Persulfate [1]
9613	0.35 0.30 0.40	0.35	9.51	40.00	Persulfate [1]
1615	0.38 0.25 0.50	0.38	21.92	52.00	Spectrographic
6111	0.35 0.40 0.38	0.38	4.39	52.00	Persulfate [1]
2826	0.40 0.40 0.60	0.47	19.15	88.00	Periodate [5]
6311	0.67 0.67 0.67	0.67	0.00	168.00	Persulfate [1,27,37]
3811	1.20 0.87 0.87	0.98	14.97	292.00	Periodate [5]
1215	3 to 10	---	---	---	Spectrographic


MANGANESE
AMOUNT ADDED = 0.25 MG/L
AVERAGE AMOUNT RECOVERED = 0.28 MG/L
MEAN
AMOUNT ADDED
MG/L
0.37
0.35
0.33
0.31
0.29
0.27
0.25
0.23
0.21
0.19
0.17
0.15
0.13
LEGEND:
PERSULFATE
PERIODATE
SPECTROGRAPH
NOT SPECIFIED
38 38 47 67 98
2111 1924 8423 9223 2411 4711 5311 4511 3211 7522 8613 4811 6211 3111 5221 1311 6411 1211 5811 7112-a 7622 8512 6512 7112-b 1811 2211 7912 9713 1711-C 5511 5611 1911 3526 4321 4421 5711 8222 1711-B 8812-B 3511 3611 3911 9113 1711-A 7222 3226 1611 2611 5111 8112 6911 9613 1615 6111 2826 6311 3811
LABORATORY NUMBER

Copper (0.42 mg/l)

The copper determination is one of the more important measurements made in the heavy metals group. The sixty-seven laboratories who reported the copper analysis used nine different procedures. The most popular was the "Cuprethol", which produced the greatest accuracy as shown by the agreement of mean, median, and amount added. The precision, however, was the poorest of the colorimetric procedures and only the results obtained with a spectrograph show greater scatter. The second most popular was the "Diethyldithiocarbamate" procedure. This method shows greater precision but tends to produce results slightly high even though normally distributed. The "Neocuproine" procedure, used by five agencies, shows equally good precision but the data indicated a trend toward low results. The other methods were not used by enough analysts to be statistically significant. Results obtained with bis(2-hydroxyethyl) dithiocarbamate using a procedure other than the "Cuprethol", as outlined in Standard Methods, were listed as a separate group. The provision for removal of iron, which is a positive interference, may account for the superior accuracy of the "Cuprethol" procedure. Use of the polarograph by three laboratories produced results with good accuracy and precision. Additional data on the use of this technique would be valuable.

The overall accuracy was excellent but the precision, in general, leaves much to be desired.

COPPER

Summary of Data (Amount added 0.42 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Cuprethol	30	89	0.42	0.42	0.19 - 0.70	± 0.04	± 0.132	± 0.028
Diethyldithio-carbamate	17	51	0.45	0.45	0.34 - 0.62	± 0.04	± 0.070	± 0.020
Neocuproine	5	15	0.37	0.34	0.31 - 0.48	± 0.08	± 0.066	± 0.036
Bis (2-hydroxy-ethyl) dithio-carbamate	3	9	0.40	0.41	0.34 - 0.45	± 0.03	± 0.050	± 0.038
Polarograph	3	9	0.41	0.40	0.38 - 0.43	± 0.02	± 0.034	± 0.026
Spectrograph	3	5	0.61	0.41	0.29 - 1.50	± 0.13	± 0.505	± 0.627
Bathocuproine	2	6	0.39	0.39	0.37 - 0.41	± 0.01	± 0.029	± 0.030
Zincon	1	3	0.31	0.31	0.31	± 0.11	± 0.007	± 0.017
Bi-quinoline	1	3	0.40	0.40	0.40	± 0.02	± 0.029	± 0.072
Overall	67	196	0.43	0.41	0.18 - 1.50	± 0.06	± 0.122	± 0.017

Table 4. COPPER (Amount added = 0.42 mg/l)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
1115	0.12 0.20 0.24	0.19	22.79	54.76	Cuprethol	1
3911	0.25 0.25 0.25	0.25	0	40.48	Cuprethol	1
7112(b)	0.29	0.29	---	30.95	Spectrographic	
9613	0.31 0.31 0.31	0.31	0	26.19	Neocuproine	1
2211	0.32 0.30 0.31	0.31	2.16	26.19	Cuprethol	5
5811	0.31 0.30 0.31	0.31	1.06	26.19	Zincon	
5711	0.33 0.33 0.33	0.33	0	21.43	Neocuproine	1
3611(a)	0.33 0.34 0.34	0.34	0.97	19.05	Neocuproine	22,23

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
2826	0.34 0.34 0.33	0.34	0.97	19.05	Diethyldithio-carbamate [8,14]
9113	0.34 0.34 0.34	0.34	0	19.05	Bis(2-hydroxy-ethyl) dithio-carbamate [39]
7112(a)	0.35	0.35	---	16.67	Cuprethol [1]
7622	0.35 0.35 0.35	0.35	0	16.67	Cuprethol [1]
1711(c)	0.39 0.35 0.38	0.37	4.51	11.90	Bathocuproine [1]
1711(a)	0.42 0.45 0.24	0.37	22.51	11.90	Cuprethol [1]
9713	0.38 0.38 0.37	0.38	0.87	9.52	Diethyldithio-carbamate [33]
1924(b)	0.38 0.38 0.37	0.38	0.87	9.52	Diethyldithio-carbamate [5]

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1811	0.39 0.39 0.37	0.38	2.63	9.52	Cuprethol [1]
3611(b)	0.38 0.37 0.40	0.38	2.63	9.52	Polarographic
7222	0.40 0.38 0.38	0.39	2.56	7.14	Cuprethol [1]
2336	0.39 0.37 0.40	0.39	2.56	7.14	Diethyldithio-carbamate [8]
4321	0.39 0.38 0.40	0.39	1.72	7.14	Diethyldithio-carbamate
2411	0.39 0.40 0.40	0.40	0.82	4.76	Cuprethol [1]
2611(b)	0.41 0.39 0.39	0.40	2.50	4.76	Cuprethol [12]

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
3111	0.40 0.40 0.40	0.40	0	4.76	Cuprethol [5]
3526	0.40 0.40 0.40	0.40	0.00	4.76	Diethyldithio-carbamate
4116	0.38 0.43 0.39	0.40	5.00	4.76	Polarographic
4421	0.38 0.43 0.38	0.40	5.82	4.76	Bi-quinoline [27]
7912	0.40 0.39 0.40	0.40	0.82	4.76	Cuprethol [1]
4511	0.41 0.42 0.40	0.41	1.63	2.38	Bis (2-hydroxy-ethyl) dithio-carbamate [30]
1615	0.37 0.37 0.50	0.41	13.83	2.38	Spectrographic

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1211	0.43 0.42 0.39	0.41	4.07	2.38	Bathocuproine [1]
1611	0.41 0.42 0.41	0.41	0.80	2.38	Neocuproine [1]
1924(a)	0.42 0.41 0.40	0.41	1.63	2.38	Cuprethol [1]
8423	0.41 0.41 0.41	0.41	0	2.38	Diethyldithio-carbamate
5511	0.41 0.43 0.42	0.42	1.60	0.00	Diethyldithio-carbamate [33]
1911	0.42 0.42 0.42	0.42	0.00	0.00	Cuprethol [1]
6311	0.42 0.42 0.42	0.42	0.00	0.00	Cuprethol [1,35]

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
7522	0.42 0.43 0.42	0.42	0.78	0.00	Cuprethol [1]
6512	0.43 0.43 0.43	0.43	0.00	2.38	Cuprethol [1]
2611(a)	0.44 0.39 0.47	0.43	6.98	2.38	Polarographic
6911	0.43 0.43 0.42	0.43	0.77	2.38	Cuprethol [1]
1711(b)	0.45 0.42 0.44	0.44	2.27	4.76	Cuprethol [1]
2111	0.44 0.44 0.45	0.44	0.75	4.76	Cuprethol [1]
6411	0.45 0.45 0.44	0.45	0.73	7.14	Diethyldithio-carbamate [5]

Table 4 (Continued)

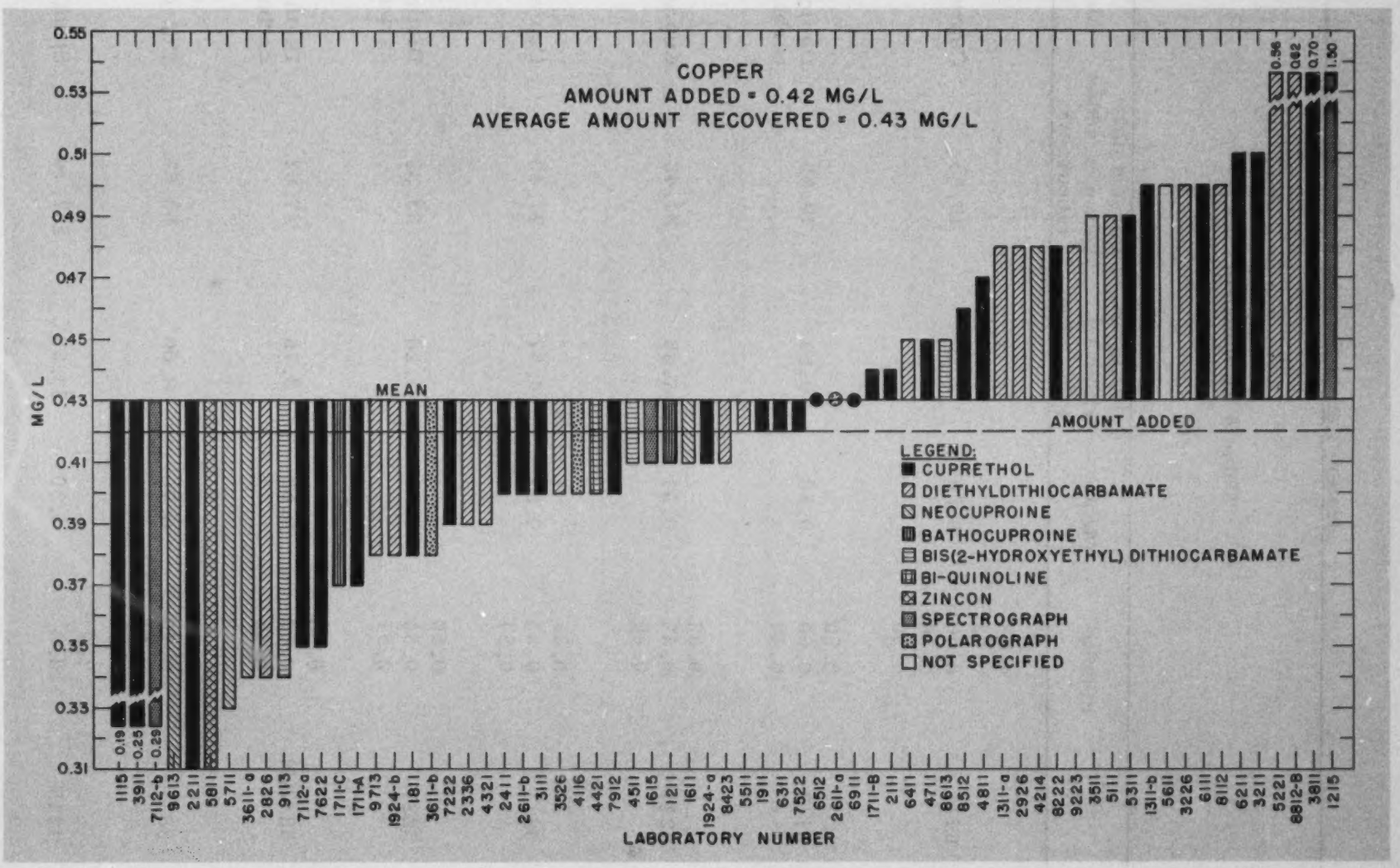
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
4711	0.44 0.44 0.46	0.45	2.22	7.14	Cuprethol [1]
8613	0.46 0.45 0.45	0.45	0.73	7.14	Bis (2-hydroxy-ethyl) dithio-carbamate [39]
8512	0.45 0.47	0.46	2.17	9.52	Cuprethol [1]
4811	0.46 0.47 0.48	0.47	1.42	11.90	Cuprethol [5]
1311(a)	0.48 0.48 0.48	0.48	0	14.28	Diethyldithio-carbamate [1]
2926	0.47 0.48 0.50	0.48	2.08	14.28	Diethyldithio-carbamate [15]
4214	0.48 0.48 0.48	0.48	0.00	14.28	Neocuproine [23]
8222	0.47 0.48 0.48	0.48	0.69	14.28	Cuprethol [1]

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
9223	0.48 0.48 0.48	0.48	0.00	14.28	Diethyldithio-carbamate [5]
3511	0.52 0.48 0.48	0.49	3.41	16.67	Unspecified [1]
5111	0.50 0.49 0.49	0.49	0.67	16.67	Diethyldithio-carbamate [5]
5311	0.49 0.49 0.50	0.49	0.67	16.67	Cuprethol [1]
1311(b)	0.50 0.50 0.50	0.50	0.00	19.05	Cuprethol [1]
5611	0.49 0.49 0.52	0.50	2.66	19.05	Unspecified
3226	0.50 0.50 0.50	0.50	0.00	19.05	Diethyldithio-carbamate [5]

Table 4 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6111	0.49 0.52 0.50 0.50 0.50	0.50	1.20	19.05	Cuprethol [1]
8112	0.50 0.50 0.49	0.50	0.66	19.05	Diethyldithio-carbamate [5]
6211	0.52 0.52 0.50	0.51	1.96	21.43	Cuprethol [1]
3211	0.48 0.55 0.51	0.51	4.57	21.43	Cuprethol [1]
5221	0.56 0.55 0.57	0.56	1.20	33.33	Diethyldithio-carbamate [5]
8812(b)	0.60 0.60 0.65	0.62	3.76	47.62	Diethyldithio-carbamate [5]
3811	0.70 0.70 0.70	0.70	0.00	66.67	Cuprethol [1]
1215	1.0 2.0	1.50	33.33	257.14	Spectrographic


COPPER
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AVERAGE AMOUNT RECOVERED = 0.43 MG/L
MEAN
AMOUNT ADDED
MG/L
LABORATORY NUMBER
LEGEND:
CUPRETHOL
DIETHYLDITHIOCARBAMATE
NEOCUPROINE
BATHOCUPROINE
BIS(2-HYDROXYETHYL) DITHIOCARBAMATE
BI-QUINOLINE
ZINCON
SPECTROGRAPH
POLAROGRAPH
NOT SPECIFIED

Iron (0.62 mg/l)

The determination of iron in a sample of this type having no organic material or turbidity should present little difficulty. Variability and instability of the sample, however, may limit the precision and accuracy of this determination more than will the errors of the analysis. As shown by the bar graph, the results are nearly all on the low side but are distributed normally except for two extremely high average values. The mean of all results is 0.16 mg/l below the amount added, which is significant from the standpoint of accuracy. A possible explanation is the formation of a colloidal precipitate which adheres to the sample bottle. This problem can be acute with plastic bottles. In an attempt to verify this assumption, bottles of sample were agitated vigorously on a shaking machine for three hours and then analyzed for iron. Comparison of the results with those obtained from unshaken bottles disclosed that failure to shake the bottle vigorously produced results averaging 0.07 mg/l lower. As a matter of further interest, determinations were made with and without hydroxylamine, using the phenanthroline procedure. The results indicated that a lack of proper reduction produced results averaging 0.05 mg/l lower on the unshaken samples, and 0.09 mg/l lower on the shaken samples. One of the participating laboratories provided analytical data obtained over a span of six months. These data show an apparent decrease in iron in proportion to the age of the sample.

It appears that part of the iron became oxidized to a form difficult to recover from the sample bottle. Interpretation of the data with respect to accuracy, therefore, can be only relative for comparison of methods.

IRON

Summary of Data (Amount added 0.62 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Phenanthroline	37	107	0.45	0.47	0.08 - 1.12	± 0.15	± 0.140	± 0.027
Thiocyanate	8	24	0.44	0.46	0.20 - 0.75	± 0.15	± 0.141	± 0.060
Tripyridine	5	14	0.46	0.46	0.34 - 0.55	± 0.14	± 0.076	± 0.044
Bipyridine	5	15	0.24	0.25	0.16 - 0.34	± 0.37	± 0.060	± 0.033
Thioglycolic Acid	3	9	0.40	0.40	0.20 - 0.68	± 0.22	± 0.171	± 0.131
Batho-phenanthroline	1	3	0.19	0.19	0.19	± 0.43	--	--
Spectrograph	2	3	0.65	0.75	0.46 - 0.75	± 0.13	± 0.481	± 1.195
Overall	64	184	0.44	0.45	0.08 - 1.24	± 0.18	± 0.177	± 0.026

Table 5. IRON (0.62 mg/1 added)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1711(a)	0.18 0.18 0.08	0.15	28.89	75.81	Phenanthroline [1]
8613	0.16 0.16 0.16	0.16	0.00	74.19	Bipyridine [39]
4214	0.19 0.19 0.19	0.19	0.00	69.35	Batho-Phenanthroline [26]
3111	0.20 0.20 0.20	0.20	0.00	67.74	Thiocyanate [3]
2336	0.20 0.21 0.22	0.21	3.17	66.13	Thioglycolic Acid [8,9]
9113	0.20 0.23 0.20	0.21	6.35	66.13	Bipyridine [39]
8112	0.19 0.28 0.22 0.22	0.23	12.17	63.31	Phenanthroline [1]

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6512	0.24 0.24 0.23	0.24	1.39	61.83	Phenanthroline[1]
8423	0.24 0.25 0.25	0.25	1.33	60.21	Bipyridine
1924	0.28 0.26 0.28	0.27	3.70	55.91	Bipyridine[3]
1711(c)	0.28 0.20 0.40	0.29	24.14	52.69	Phenanthroline[1]
1611	0.30 0.30 0.30	0.30	0.00	51.61	Thiocyanate[3]
1211	0.32 0.32 0.31	0.32	1.04	48.92	Phenanthroline[1]
1711(b)	0.22 0.40 0.30	0.33	21.21	50.54	Phenanthroline[1]

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1811	0.34 0.32 0.33	0.33	2.02	46.77	Phenanthroline Extraction
1911(a)	0.33 0.33 0.32	0.33	1.01	47.31	Phenanthroline
1911(b)	0.34 0.32 0.33	0.33	2.02	46.77	Bipyridine
2926	0.35 0.35 0.35	0.35	0.00	43.55	Phenanthroline
7522	0.34 0.36 0.35	0.35	1.90	43.55	Phenanthroline & Tripyridine
5711	0.38 0.35 0.35	0.36	3.70	41.94	Phenanthroline
7222	0.38 0.40 0.34	0.37	6.30	39.78	Phenanthroline

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
7112	0.37 0.39	0.38	2.63	38.71	Phenanthroline
3526	0.37 0.40 0.40	0.39	3.42	37.10	Thioglycolic Acid
5811	0.40 0.40 0.40	0.40	0.00	35.48	Thiocyanate
8222	0.40 0.40 0.40	0.40	0.00	35.48	Phenanthroline
1115	0.46 0.44 0.40	0.43	5.42	30.11	Phenanthroline
2611	0.43 0.43 0.43	0.43	0.00	30.64	Tripyridine
3511	0.46 0.42 0.42	0.43	3.87	30.11	Unspecified

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6911	0.44 0.43 0.44	0.44	0.76	28.49	Phenanthroline [1]
7912	0.45 0.44 0.45	0.45	0.74	27.96	Phenanthroline [1]
4811	0.47 0.47 0.45	0.46	2.17	25.27	Phenanthroline [5]
5111	0.48 0.45 0.45	0.46	2.90	25.81	Thiocyanate [3]
7112	0.46	0.46	---	25.81	Spectrographic
4321	0.45 0.47 0.48	0.47	2.13	24.73	Thiocyanate
4711	0.46 0.48 0.46	0.47	2.13	24.73	Tripyridine [1]
9223	0.47 0.47 0.47	0.47	0.00	24.19	Phenanthroline [1]

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
2211	0.50 0.45 0.50	0.48	4.86	22.04	Phenanthroline	5
5221	0.48 0.48 0.49	0.48	0.69	22.04	Phenanthroline	1
3211	0.49 0.49 0.50	0.49	0.68	20.43	Phenanthroline	5
4511	0.50 0.50 0.50	0.50	0.00	19.35	Phenanthroline	1
2411	0.51 0.50 0.50	0.50	0.67	18.82	Phenanthroline	1
3811	0.50 0.50 0.50	0.50	0.00	19.35	Thiocyanate	1
6411	0.52 0.50 0.54	0.52	2.56	16.13	Thiocyanate	3

Table 5 (Continued)

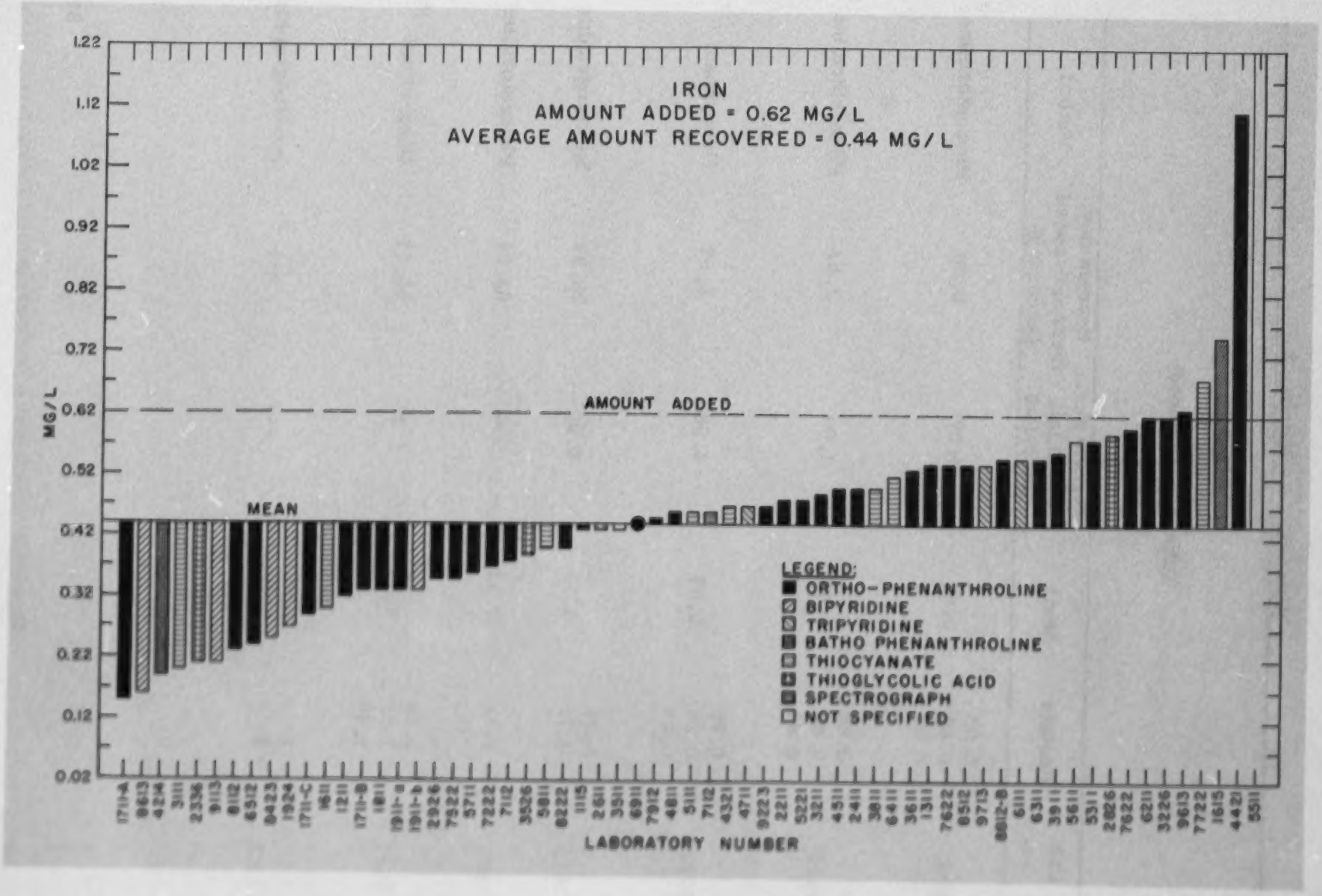
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
3611	0.52 0.54 0.54	0.53	1.89	13.98	Phenanthroline [1]
1311	0.53 0.54 0.55	0.54	1.23	12.90	Phenanthroline [1]
7622	0.53 0.55	0.54	1.85	12.90	Phenanthroline [1]
8512	0.55 0.54 0.54	0.54	0.62	12.36	Phenanthroline [1]
9713	0.54 0.54	0.54	0.00	12.90	Tripyridine [1]
8812(b)	0.56 0.54 0.55	0.55	1.21	11.29	Phenanthroline [5]
6111	0.54 0.55 0.55	0.55	0.60	11.83	Tripyridine [1]

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6311	0.56 0.54 0.56	0.55	1.82	10.75	Phenanthroline [1,36]
3911	0.56 0.56 0.56	0.56	0.00	9.68	Phenanthroline [1]
5611	0.54 0.60 0.60	0.58	4.60	6.45	Unspecified
5311	0.58 0.58 0.57	0.58	0.57	6.99	Phenanthroline [1]
2826	0.68 0.48 0.60	0.59	11.86	11.83	Thioglycolic Acid
7622	0.58 0.61	0.60	2.50	4.03	Phenanthroline Extraction [1]
6211	0.64 0.62 0.60	0.62	2.15	0.00	Phenanthroline [1]

Table 5 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
3226	0.63 0.62 0.61	0.62	1.07	0.00	Phenanthroline
9613	0.60 0.64 0.64	0.63	2.69	1.61	Phenanthroline
7722	0.75 0.65 0.65	0.68	6.98	9.68	Thiocyanate
1615	0.75 0.75	0.75	0.00	20.97	Spectrographic
4421	1.12	1.12	---	80.64	Phenanthroline
5511	1.24 1.22 1.19	1.22	1.37	96.77	Unspecified
1215	$> 2^3$	---	---	---	Spectrographic


IRON
AMOUNT ADDED = 0.62 MG/L
AVERAGE AMOUNT RECOVERED = 0.44 MG/L
MG/L
1.22
1.12
1.02
0.92
0.82
0.72
0.62
0.52
0.42
0.32
0.22
0.12
0.02
AMOUNT ADDED
MEAN
LEGEND:
ORTHO-PHENANTHROLINE
BIPYRIDINE
TRIPYRIDINE
BATHO PHENANTHROLINE
THIOCYANATE
THIOGLYCOLIC ACID
SPECTROGRAPH
NOT SPECIFIED
1711-A
9613
424
3111
2336
9113
8112
6512
0423
1924
1711-C
911
1211
1711-B
1811
1911-B
1911-A
2926
7922
5711
7222
7112
3526
5911
8222
1115
2611
3511
6911
7912
4811
511
7112
4321
4711
9223
2211
5221
3211
4511
2411
3811
6411
3611
1311
7622
8512
9713
8812-B
6111
6311
3911
5611
5311
2826
7622
6211
3226
9613
7722
1615
4421
5511
LABORATORY NUMBER

Cadmium (0.24 mg/l)

Of the eight metals contained in this sample, cadmium is generally considered the most difficult to measure. Since many of these metals react with dithizone, it is reasonable to expect positive errors due to incomplete removal or complexing of interfering metals. This trend is indicated in the bar graph which shows a slightly skewed distribution. Dithizone was employed by 30 agencies, while only three used the polarograph, two used the spectrograph, one used the "cadion" procedure, and two did not report the method used. As a consequence, statistical comparison of methods is somewhat inconclusive. On the basis of nine results reported by three laboratories using the polarograph, it appears that this technique is sufficiently precise and accurate for routine work. The spectrograph, on the other hand, does not appear to be suitable for the measurement of cadmium at the concentration present in this sample.

CADMIUM

Summary of Data (Amount added 0.24 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Dithizone	30	84	0.27	0.25	0.04 - 0.70	± 0.04	± 0.099	± 0.022
Polarograph	3	9	0.26	0.27	0.21 - 0.32	± 0.03	± 0.041	± 0.032
Spectrograph	2	4	0.27	0.28	0.03 - 0.50	± 0.21	± 0.263	± 0.418
Cadion	1	3	0.21	0.21	0.20 - 0.22	± 0.03	± 0.010	± 0.025
Overall	38	105	0.26	0.24	0.03 - 0.70	± 0.04	± 0.101	± 0.020

Table 6. CADMIUM (Amount Added = 0.24 mg/l)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
1611	0.04 0.04	0.04	0.00	83.33	Dithizone	1
1215	0.03 0.06	0.04	37.50	83.33	Spectrographic	
6311	0.08 0.08 0.08	0.08	0.00	66.67	Dithizone	1
1711	0.22 0.17 0.15	0.18	14.83	25.00	Dithizone	1
4421	0.18 0.21 0.22	0.20	8.35	16.67	Dithizone	27
7622	0.20 0.20 0.20	0.20	0.00	16.67	Dithizone	1
8512	0.20 0.19	0.20	2.50	16.67	Dithizone	1
4116	0.21 0.21 0.22	0.21	1.57	12.50	Polarographic	
4811	0.22 0.20 0.21	0.21	3.19	12.50	"Cadion"	31

Table 6 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
5511	0.22 0.22 0.23	0.22	1.50	8.33	Dithizone [1]
3816	0.22 0.22 0.21 0.23	0.22	2.27	8.33	Not specified
3511	0.22 0.22 0.22	0.22	0.00	8.33	Dithizone [19]
1211	0.23 0.23 0.23	0.23	0.00	4.17	Dithizone [2]
3211	0.24 0.25 0.23	0.24	2.79	0	Dithizone [2]
5611	0.24	0.24	---	0	Unspecified
1811	0.23 0.24 0.24	0.24	1.38	0	Dithizone [1]
3111	0.23 0.25 0.24	0.24	2.79	0	Dithizone [1]

Table 6 (Continued)

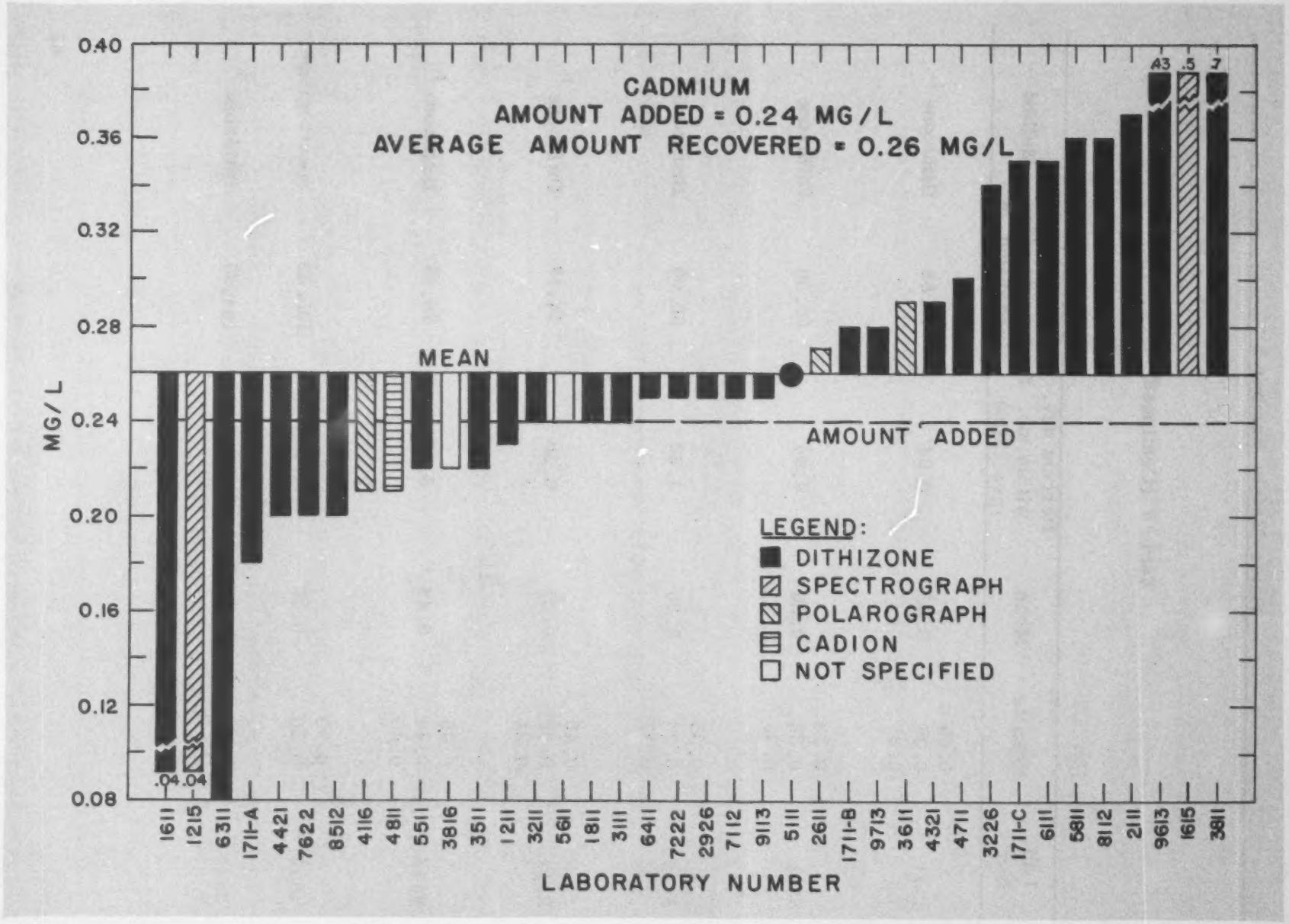
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6411	0.25 0.25 0.24	0.25	1.32	4.17	Dithizone [2]
7222	0.28 0.30 0.16	0.25	22.68	4.17	Dithizone [1]
2926	0.25 0.25 0.24	0.25	1.32	4.17	Dithizone [2]
7112 (a)	0.28 0.23 0.25	0.25	6.68	4.17	Dithizone [1]
9113	0.24 0.25 0.25	0.25	1.32	4.17	Dithizone
5111	0.24 0.27 0.26	0.26	3.85	8.33	Dithizone [27]
2611	0.27 0.23 0.32	0.27	11.11	12.50	Polarographic

Table 6 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
1711 (b)	0.30 0.27 0.26	0.28	5.96	16.67	Dithizone	2
9713	0.27 0.30	0.28	5.36	16.67	Dithizone	1
3611	0.29 0.28 0.29	0.29	1.14	20.83	Polarographic	24
4321	0.28 0.30	0.29	3.45	20.83	Dithizone	
4711	0.30 0.30 0.29	0.30	1.10	25.00	Dithizone	1
3226	0.34 0.34 0.34	0.34	0.00	41.67	Dithizone	1
1711 (c)	0.23 0.24 0.58	0.35	43.80	45.83	Dithizone	2

Table 6 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6111	0.36 0.35 0.35	0.35	0.94	45.83	Dithizone [1]
5811	0.33 0.38 0.36	0.36	4.64	50.00	Dithizone
8112	0.35 0.36 0.37	0.36	1.86	50.00	Dithizone [1]
2111	0.40 0.38 0.34	0.37	6.30	54.17	Dithizone [1]
9613	0.40 0.41 0.49	0.43	8.53	79.17	Dithizone [1]
1615	0.50 0.50	0.50	0.00	108.33	Spectrographic
3811	0.70	0.70	---	191.67	Dithizone [1]


CADMIUM
AMOUNT ADDED = 0.24 MG/L
AVERAGE AMOUNT RECOVERED = 0.26 MG/L
MEAN
AMOUNT ADDED
MG/L
0.40
0.36
0.32
0.28
0.24
0.20
0.16
0.12
0.08
.04
.04
A3
.5
.7
LEGEND:
DITHIZONE
SPECTROGRAPH
POLAROGRAPH
CADION
NOT SPECIFIED
1611
1215
6311
1711-A
4421
7622
8512
4116
4811
5511
3816
3511
1211
3211
5611
1811
3111
6411
7222
2926
7112
9113
5111
2611
1711-B
9713
3611
4321
4711
3226
1711-C
6111
5811
8112
2111
9613
1615
3811
LABORATORY NUMBER

Zinc (0.90 mg/l)

Most of the participants performing the zinc analysis reported using dithizone. Fourteen used a mixed color method, 18 used a monocolor procedure, and four reported only that they used dithizone. The results reported by three laboratories using the spectrograph were all below the amount added and were widely divergent. Better results were obtained by three participants using the polarograph, but they, likewise, exhibit a tendency to be slightly low. The mixed color dithizone results show the best accuracy and precision and are equally distributed above and below the overall mean. If the exceptionally low results reported by the lowest participant are discarded, the standard deviation for this method is reduced from $\pm$ 0.237 to $\pm$ 0.114, and the mean is raised from 0.84 to 0.90, which was the amount added. Several accurate results were obtained with the monocolor dithizone procedures, but, in general, the results tend to be high and widely scattered. Results obtained by five laboratories with zincon are well distributed about the mean but exhibit a lack of precision.

ZINC

Summary of Data (Amount added 0.90 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Dithizone Mixed color	14	42	0.84	0.94	0.09 - 1.00	± 0.07	± 0.237	± 0.074
Dithizone Monocolor	18	53	1.02	0.94	0.40 - 2.30	± 0.18	± 0.374	± 0.103
Dithizone Unspecified	4	11	1.19	1.14	0.80 - 1.80	± 0.24	± 0.319	± 0.214
Zincon	5	15	0.93	0.83	0.70 - 1.21	± 0.18	± 0.210	± 0.116
Polarograph	3	9	0.76	0.83	0.50 - 0.97	± 0.07	± 0.197	± 0.151
Spectrograph	3	5	0.67	0.68	0.30 - 1.00	± 0.22	± 0.254	± 0.315
Overall	48	136	0.94	0.94	0.09 - 2.30	± 0.15	± 0.318	± 0.054

Table 7. ZINC (Amount added = 0.90 mg/l)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
5511	0.10 0.09 0.10	0.10	3.30	88.89	Mixed Color [1]
1215	0.30 0.60	0.45	33.33	50.00	Spectrograph
3211	0.54 0.40 0.50	0.48	11.10	46.67	Mono Color [1]
2611	0.53 0.50 0.50	0.51	2.61	43.33	Polarographic
7222	0.48 0.60 0.46	0.51	11.12	43.33	Mono Color [1]
2111	0.64 0.63 0.63	0.63	0.52	30.00	Mixed Color [1]
7112 (b)	0.68	0.68	---	24.44	Spectrographic

Table 7 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1711(c)	0.79 0.74 0.57	0.70	12.38	22.22	Mixed Color [1]
7112(a)	0.70	0.70	---	22.22	Mono Color [1]
9713	0.70 0.72 0.74	0.72	1.85	20.00	Zincon
4421	0.89 0.52 0.78	0.73	19.18	18.89	Mono Color [28,29]
8512	0.73 0.75	0.74	1.35	17.78	Mixed Color [1]
5811	0.75 0.78 0.75	0.76	1.75	15.56	Zincon
3611	0.83 0.83 0.79	0.82	2.04	8.89	Polarographic [24]
4511	0.80 0.84 0.86	0.83	2.81	7.78	Mono Color [1]

Table 7 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
3226	0.86 0.83 0.80	0.83	2.41	7.78	Zincon [16]
8112	0.87 0.87 0.87	0.87	0.00	3.33	Mono Color [1]
1615	1.0 0.75	0.88	13.64	2.22	Spectrographic
1311(a)	0.91 0.92 0.90	0.91	0.74	1.11	Mixed Color [1]
1811	0.91 0.88 0.94	0.91	2.20	1.11	Mono Color [1]
1611	0.87 0.96 0.89	0.91	4.03	1.11	Mono Color [1]
3111	0.92 0.92 0.90 0.90	0.91	1.10	1.11	Mixed Color [1]

Table 7 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1711(a)	0.94 0.97 0.85	0.92	5.08	2.22	Mixed Color [1]
4321	0.94 0.92 0.90	0.92	1.44	2.22	Mono Color
4811	0.94 0.96 0.92	0.94	1.41	4.44	Mono Color
1211	0.92 0.94 0.96	0.94	1.41	4.44	Mixed Color [1]
3811	0.80 1.10	0.95	15.79	5.55	Dithizone Unspecified
4116	0.97 0.96 0.93	0.95	1.76	5.55	Polarographic
9113	0.93 0.94 0.99	0.95	2.45	5.55	Mixed Color [3]

Table 7 (Continued)

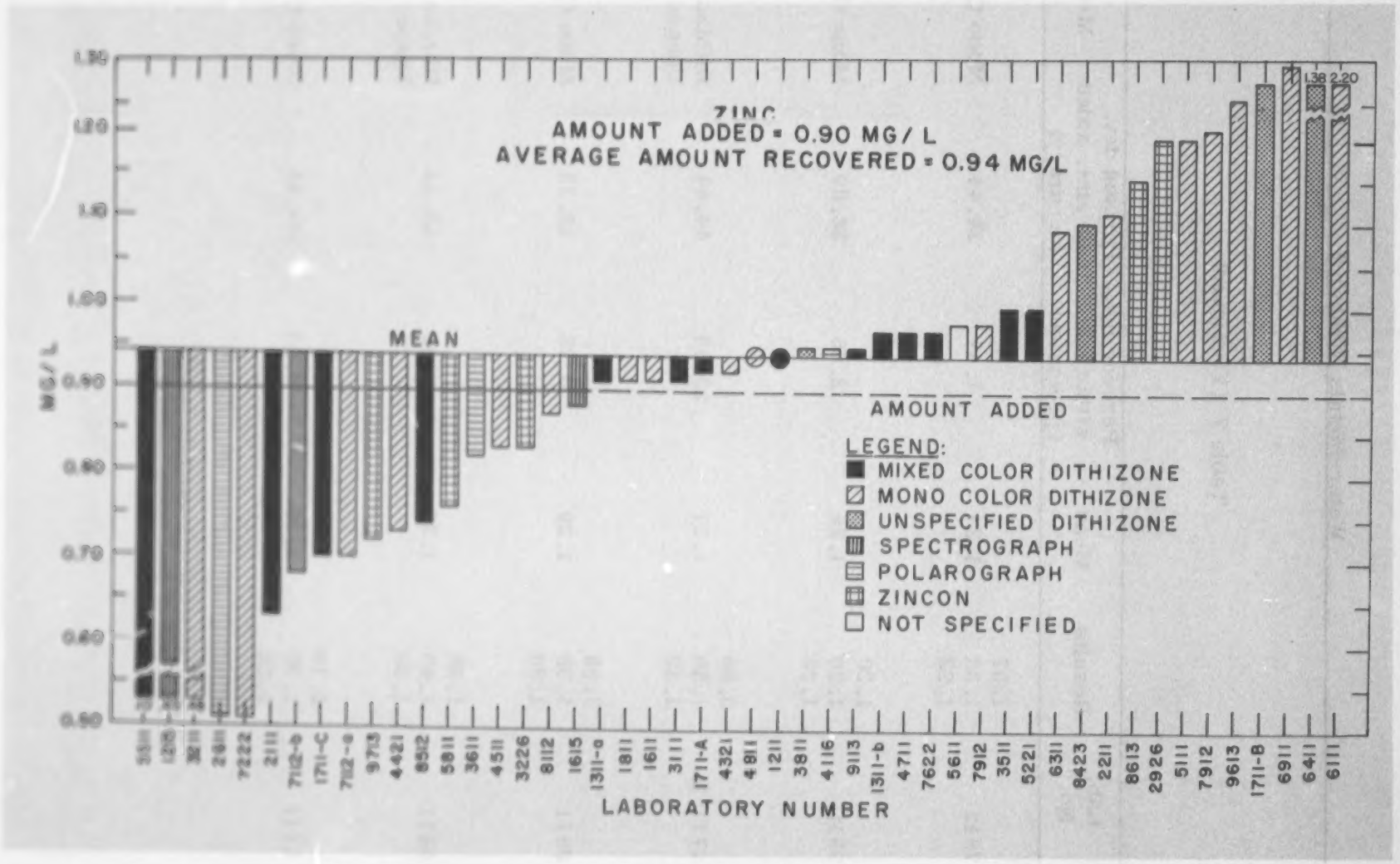
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
1311(b)	0.96 0.98 0.96	0.97	1.03	7.78	Mixed Color	1
4711	1.00 0.96 0.94	0.97	2.40	7.78	Mixed Color	1
7622	1.00 0.97 0.95	0.97	1.72	7.78	Mixed Color	1
5611	0.98	0.98	---	8.89	Unspecified	
7912	1.00 0.93 1.00	0.98	3.06	8.89	Mono Color	1
2311	1.00 1.00 1.00	1.00	0.00	11.11	Mixed Color	1
1221	1.00 1.00 1.00	1.00	0.00	11.11	Mixed Color	5

Table 7 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
6311	1.08 1.09 1.09 1.09	1.09	0.23	21.11	Mono Color [1,27]
8423	1.10 1.14 1.05	1.10	2.73	22.22	Dithizone Unspecified
2211	1.08 1.08 1.17	1.11	3.60	23.33	Mono Color [7]
8613	1.17 1.16 1.12	1.15	1.74	27.78	Zincon [16]
2926	1.18 1.21 1.20	1.20	0.83	33.33	Zincon [16]
5111	1.17 1.22 1.20	1.20	1.39	33.33	Mono Color [27]

Table 7 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
7912	1.07 1.33 1.22	1.21	7.44	34.44	Mono Color	I
9613	1.30 1.20 1.25	1.25	2.66	38.89	Mono Color	I
1711(b)	0.80 1.80 1.20	1.27	28.03	44.44	Dithizone Unspecified	I
6911	1.28 1.30 1.30	1.29	0.78	43.33	Mono Color	I
6411	1.36 1.40 1.38	1.38	0.96	53.33	Dithizone Unspecified	
6111	2.10 2.30 2.20	2.20	3.03	144.44	Mono Color	I


ZINC
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AVERAGE AMOUNT RECOVERED = 0.94 MG/L
MEAN
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MG/L
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2.20
LEGEND:
MIXED COLOR DITHIZONE
MONO COLOR DITHIZONE
UNSPECIFIED DITHIZONE
SPECTROGRAPH
POLAROGRAPH
ZINCON
NOT SPECIFIED
LABORATORY NUMBER

Lead (0.18 mg/l)

The only colorimetric reagent used for the analysis of lead was dithizone, but many modifications in procedure were employed. From the information supplied by participants, an effort was made to arrange the results into two main groups. Of the 46 agencies performing the analysis, 22 used a mixed color method, essentially the same as outlined in Standard Methods. Nine laboratories used the monocolor procedure, and nine used dithizone without specifying the method. One laboratory used a modification, designed for the determination of lead in urine and blood, which was treated as a separate method.

The best accuracy and precision were shown by the mixed color procedure. The monocolor results tend to be a little high and a little less precise, as indicated by the larger values for standard deviation and 95% confidence limits.

Three results provided by one laboratory using the polarograph were reasonably accurate and precise. It is unfortunate that this technique was not used by enough analysts to provide a statistically sound evaluation.

Three results provided by two laboratories using the spectrograph show excessive scatter and, although the mean value is quite accurate, the value of this technique for low concentration lead analysis is questionable.

In general, the mixed color dithizone procedure appears to be the most desirable technique for the analysis of lead at low concentration.

LEAD

Summary of Data (Amount added 0.18 mg/l)

Method	Number of users	Number of results	Mean	Median	Range	50% range	Standard deviation	95% Confidence limits
Mixed color Dithizone	22	64	0.19	0.18	0.02 - 0.40	± 0.03	± 0.060	± 0.015
Modified Dithizone	1	3	0.14	0.14	0.13 - 0.14	± 0.04	± 0.007	± 0.017
Mono color Dithizone	9	25	0.21	0.20	0.10 - 0.38	± 0.03	± 0.068	± 0.028
Unspecified Dithizone	9	27	0.22	0.22	0.15 - 0.29	± 0.03	± 0.038	± 0.015
Polarograph	1	3	0.20	0.21	0.18 - 0.21	± 0.03	± 0.017	± 0.042
Spectrograph	2	3	0.19	0.20	0.10 - 0.27	± 0.09	± 0.085	± 0.211
Overall	46	129	0.20	0.20	0.02 - 0.40	± 0.03	± 0.055	± 0.010

Table 8. LEAD (0.18 mg/1 added)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
1711(a)	0.18 0.16 0.02	0.12	55.58	37.06	Mixed Color[1]
9613	0.14 0.10 0.12	0.12	11.08	33.33	Mono Color[1]
3611	0.14 0.14 0.13	0.14	2.36	24.06	Modified Dithizone Mixed Color
4711	0.15 0.14 0.14	0.14	2.36	20.39	Mixed Color[1]
1311	0.14 0.15 0.15	0.15	2.20	18.50	Mixed Color
1711(c)	0.10 0.18 0.17	0.15	22.20	16.67	Mixed Color[1]
1215	0.1 0.2	0.15	33.33	16.50	Spectrograph

Table 8 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
4933	0.15 0.15 0.14	0.15	2.20	18.50	Mixed Color	
5811	0.16 0.15 0.14	0.15	4.47	16.67	Mixed Color	1
7912	0.15 0.15 0.15	0.15	0.00	16.67	Mixed Color	1
5511	0.16 0.16 0.16	0.16	0.00	11.11	Mixed Color	1
8613	0.16 0.15 0.16	0.16	2.06	12.94	Mixed Color	39
3111	0.17 0.16	0.16	3.12	8.33	Mixed Color	1
3511	0.17 0.17 0.16	0.17	1.94	7.39	Unspecified	20

Table 8 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
1711(b)	0.15 0.18 0.20	0.18	9.28	9.28	Dithizone Unspecified	1
3211	0.20 0.18 0.17	0.18	5.56	5.56	Mixed Color	1
3226	0.19 0.18 0.18	0.18	1.83	1.83	Mixed Color	1
3811	0.18 0.19 0.18	0.18	1.83	1.83	Mono Color	25
6411	0.18 0.20 0.20	0.19	5.26	7.39	Dithizone Unspecified	
7222	0.17 0.19 0.20	0.19	5.26	7.39	Mono Color	1
1211	0.19 0.19 0.20	0.19	1.74	7.39	Mixed Color	1

Table 8 (Continued)

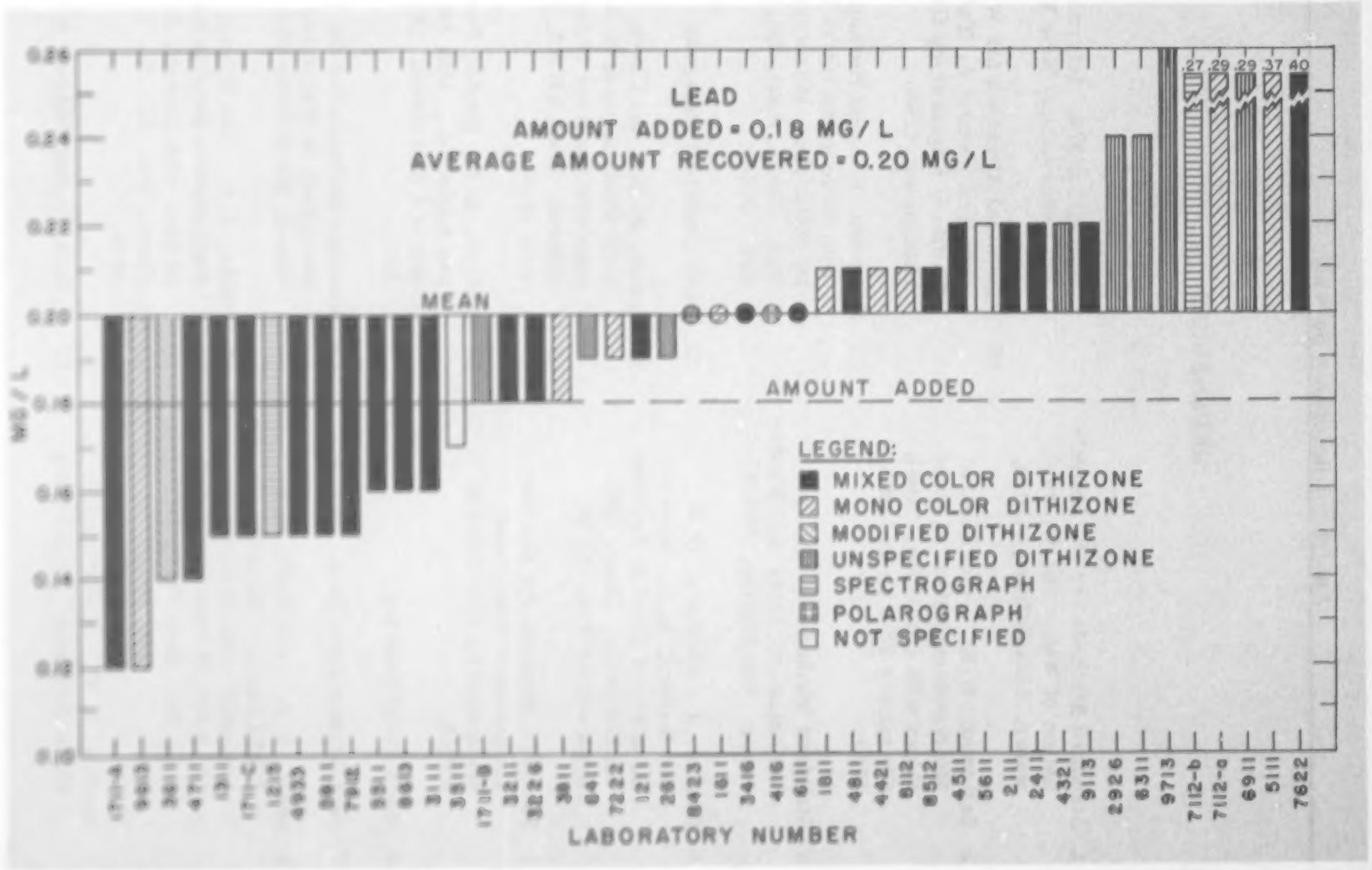
Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method
2611	0.20 0.20 0.17	0.19	7.00	9.28	Dithizone [1] Unspecified
8423	0.20 0.20 0.20	0.20	0.00	11.11	Dithizone Unspecified
1611	0.20 0.19 0.21	0.20	3.35	11.11	Mono Color [4]
3416	0.20 0.20 0.20	0.20	0.00	11.11	Mixed Color [9,18]
4116	0.21 0.21 0.18	0.20	6.65	11.11	Polarographic
6111	0.20 0.19 0.20	0.20	1.65	9.28	Mixed Color [1]
1811	0.20 0.21 0.21	0.21	1.57	14.83	Mono Color [1]

Table 8 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
4811	(.24 (.18 (.20	0.21	11.10	14.77	Mixed Color	
4421	(.23 (.19 (.20	0.21	7.90	14.77	Mono Color	27
8112	(.21 (.22 (.21	0.21	1.57	18.50	Mono Color	1
8512	(.20 (.22	0.21	4.76	16.66	Mixed Color	5
4511	.23 .21 .23	0.22	4.54	24.05	Mixed Color	
5611	.22	0.22	---	22.22	Unspecified	
2111	.23 .21 .23	0.22	4.54	24.05	Mixed Color	1
2411	.22 .23 .21	0.22	3.00	22.22	Mixed Color	10,11

Table 8 (Continued)

Lab. No.	Results	Mean	Percent dev. within lab. (precision)	Percent dev. from amt. added (accuracy)	Method	
4321	0.21 0.22 0.22	0.22	1.50	20.33	Dithizone Unspecified	
9113	0.22 0.21 0.24	0.22	4.54	24.05	Mixed Color	39
2926	0.24 0.24 0.24	0.24	0.00	33.33	Dithizone Unspecified	1
6311	0.24 0.26 0.22	0.24	5.54	33.33	Dithizone Unspecified	1,27
9713	0.24 0.26 0.29	0.26	6.38	46.27	Dithizone Unspecified	
7112 (b)	0.27	0.27	---	50.00	Spectrographic	
7112 (a)	0.29	0.29	---	61.11	Mono Color	1
6911	0.29 0.29 0.29	0.29	0.00	61.11	Dithizone Unspecified	1
5111	0.38 0.35 0.34	0.37	4.48	103.7	Mono Color	27
7422	0.40 0.40 0.40	0.40	0.00	122.2	Mixed Color	1


LEAD
AMOUNT ADDED = 0.18 MG/L
AVERAGE AMOUNT RECOVERED = 0.20 MG/L
MEAN
AMOUNT ADDED
MG/L
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
.27 .29 .29 .37 .40
LEGEND:
MIXED COLOR DITHIZONE
MONO COLOR DITHIZONE
MODIFIED DITHIZONE
UNSPECIFIED DITHIZONE
SPECTROGRAPH
POLAROGRAPH
NOT SPECIFIED
LABORATORY NUMBER

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Massachusetts Department of Public Health
Massachusetts General Hospital
Michigan State Department of Health
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Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health
Nevada State Department of Health (Las Vegas)
Nevada State Department of Health (Reno)

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New Jersey State Department of Health
New Mexico State Department of Public Health
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Vancouver B. C., Canada, Department of National Health and Welfare